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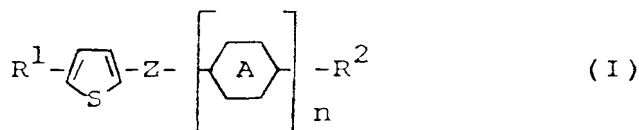
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(54) Alkylthiophenes

(57) Alkylthiophenes of the formula I



wherein

R<sup>1</sup> is alkyl with up to 16 C atoms wherein one CH<sub>2</sub> group may be replaced by -O-.

R<sup>2</sup> is X or an alkyl or alkenyl residue each with up to 16 C atoms wherein one or two non-adjacent CH<sub>2</sub> groups of these residues may be replaced by -O-, -CO-O- or -O-CO-.

Z is -CO-O-, -O-CO-, -CH<sub>2</sub>-O- or -CH<sub>2</sub>CH<sub>2</sub>-.

A is Cyc or Phe.

Cyc is trans-1, 4-cyclohexylene.

Phe is 1, 4-phenylene optionally substituted by fluorine or methyl groups.

X is F or CN, and

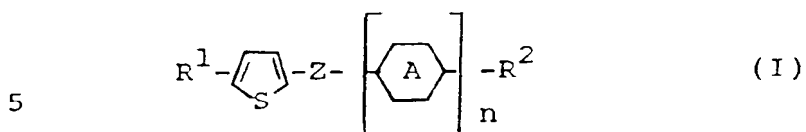
n is 1 or 2.

can be used as components of liquid crystalline media for electrooptical display devices.

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### Alkylthiophenes

1. The invention relates to alkylthiophenes of the formula I



wherein

$R^1$  is alkyl with up to 16 C atoms wherein one  $\text{CH}_2$  group may be replaced by  $-\text{O}-$ ,

10  $R^2$  is X or an alkyl or alkenyl residue each with up to 16 C atoms wherein one or two non-adjacent  $\text{CH}_2$  groups of these residues may be replaced by  $-\text{O}-$ ,  $-\text{CO}-\text{O}-$  or  $-\text{O}-\text{CO}-$ ,

Z is  $-\text{CO}-\text{O}-$ ,  $-\text{O}-\text{CO}-$ ,  $-\text{CH}_2-\text{O}-$  or  $-\text{CH}_2\text{CH}_2-$ ,

$\text{--}\text{C}_6\text{H}_4\text{A}\text{--}$  is Cyc or Phe,

15 Cyc is trans-1,4-cyclohexylene,

Phe is 1,4-phenylene optionally substituted by fluorine or methyl groups,

X is F or CN, and

n is 1 or 2.

Liquid crystal phases are commonly exhibited by organic compounds having extended rod-like molecules, and are characterised in their liquid crystalline state by a degree of order intermediate between those of a crystalline solid and of an isotropic liquid respectively. The wide-spread use of liquid crystalline materials in electro-optic devices arises from their combination of fluid-like flow with an anisotropy of their physical properties that is typical for a crystalline material. When a liquid crystal material is utilised in an electro-optic device, optimal performance can only be obtained when the physical properties of the material are adjusted to extreme or optimal values to suit the particular application and device geometry in use. Examples of the physical properties which may beneficially be changed to improve the utility of a liquid crystalline material for a particular application include such properties as the mesogenic phase range, the dielectric constants, the elastic constants, the viscosity coefficient, and the refractive indices of the material.

The present invention provides a novel family of liquid crystal compounds which may be used by themselves or in admixture with other liquid crystal compounds classes to provide mixtures having advantageous combinations of liquid crystal properties, in particular low values of refractive indices and/or birefringence. It is well known that the performance of known optical and electro-optic devices can be improved by the reduction of the refractive indices or birefringence of the liquid crystalline material contained therein. For example, in the electrooptic dis-

play based upon the twisted nematic mode of operation, the off-state transmission of light only achieves its ideal value for discrete values of the parameter  $U$  where  $U$  is defined by the relation

5 
$$U = 2D\Delta n/\lambda$$

where  $D$  is the thickness of the display cell,  $\Delta n$  is the birefringence of the liquid crystal and  $\lambda$  is the average wavelength of visible light and optimal performance in the display cell is obtained for values of  $U$  equal to  
10  $\sqrt{3}$ ,  $\sqrt{15}$ , etc. To allow use of a liquid crystalline material in a display cell it is therefore desirable that its birefringence should be adjusted so that the above equation is satisfied for the particular cell thickness which is chosen. In liquid crystal display cells containing di-  
15 chroic-dyed liquid crystal materials and operating in the cholesteric to nematic phase-change mode otherwise known as the White-Taylor mode of operation, the birefringence of the liquid crystalline host mixture leads to the undesirable propagation of elliptically polarised  
20 light rays in the display cell which diminishes the optical efficiency of the display devices. It is therefore desirable when designing liquid crystal materials for use in this type of display, to adjust the birefringence of the liquid crystalline phase to the smallest  
25 practical value in order to obtain the best performance from the display. In electro-optic switching devices in which the liquid crystal material is used on an overlay on a planar optical waveguide, or as a cladding material on a fibre waveguide, it is essential that at least one  
30 of the refractive indices of the liquid crystalline material used is lower in value than that of the waveguide material or else the structure will no longer sustain the propagation of light within the waveguide.

According to the mode of operation chosen for such a device, it may be required to have the waveguide refractive index intermediate between the two refractive indices of the liquid crystalline overlayer, or to have  
5 the refractive index of the waveguide higher than either of the refractive indices of the liquid crystalline material. In liquid crystal mixtures intended for use in the NCAP display mode the clarity of the "ON" state of the device depends upon the accurate matching of the  
10 ordinary refractive index of the LC material to the refractive index of the supporting polymer matrix. The ability to alter the absolute refractive indices of the liquid crystal therefore both facilitates the formulation of mixtures for use in this device, and offers the  
15 opportunity to utilise a wider range of supporting polymers than would otherwise be possible.

The birefringence and refractive indices of organic compounds and in particular those of liquid crystalline compounds are dependent on the electronic polarisability  
20 of the constituent molecules. Liquid crystal compounds having a largely aromatic character are commonly characterised by large values of the refractive indices and the birefringence. It has now been found unexpectedly that the compounds of formula I uniquely combine a  
25 moderately large birefringence with low absolute values of the refractive indices and further uniquely provide liquid crystalline compounds with wide nematic phase ranges having an ordinary refractive index lower than that of a fused silica wave guide at ordinary temperatures  
30 and wavelengths. The compounds can therefore be used by themselves or in combination with other classes of liquid crystalline compounds to provide mixtures in which the physical properties, particularly the refractive indices are optimised for electro-optic device applications.

The compounds of formula I can be used as components of liquid crystalline mixtures in particular for displays based on the twisted nematic and super twisted nematic cell, the effect of deformation of aligned phases or the NCAP effect, and for optical switching devices using a liquid crystal overlayer on a waveguiding substrate.

Compounds of the formula I are also suitable for use as components of chirally tilted smectic phases. Chirally tilted smectic, liquid-crystal phases having ferroelectric properties can be prepared by adding a suitable chiral doping substance to base mixtures containing one or more tilted smectic phases (L.A. Veresnev et al., Mol. Cryst. Liq. Cryst. 89, 327 (1982); H.R. Brand et al., J. Physique 44 (Lett.), L-771 (1983)). Phases of this type can be used as dielectrics for high-speed displays based on the principle described by Clark and Lagerwall of SSFLC technology (N.A. Clark and S.T. Lagerwall, Appl. Phys. Lett. 36, 899 (1980); UPS 4,367,924) based on the ferroelectric properties of the chirally tilted phase.

20 The invention was based on the object of discovering new stable partially fluorinated materials which are suitable as components of conventional liquid crystalline mixtures.

25 Liquid crystals derived from alkyl-thiophene are also  
known (D. Demus et al.; Flüssige Kristalle in Tabellen,  
VEB Deutscher Verlag für Grundstoffindustrie, Leipzig  
1974 (Vol I) and 1984 (Vol II)), but the known materials  
are derivatives of Schiff bases which suffer from  
photochemical, hydrolytic and oxidative instability  
30 rendering them unsuitable for use in electrooptic

devices. Further these compounds of the prior art show their liquid crystalline phase behaviour at very high temperature, which also makes them unsuitable for device applications.

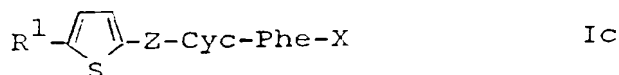
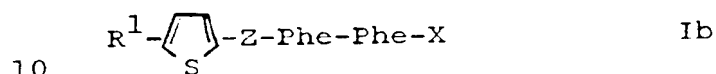
- 5 Similar thiophene derivatives are known from Sugitdinov, J.A. and Schubert, H. Zh. Org. Khim 14, 1060, (1978), from the US Patent Specification 4,659,503 or the Japanese Patent Application J 55 151 077, but these compounds exhibit a thiophene group which is directly linked to  
10 another aromatic or heteroaromatic ring. These compounds have higher absolute values of the refractive indices than the compounds according to the invention.

The compounds of formula I provide liquid crystalline compounds having their liquid crystalline phase ranges  
15 at conveniently low temperature and the standard mixing techniques known to those skilled in the art may be applied to formulate mixtures which are liquid crystalline in the room temperature region and below.

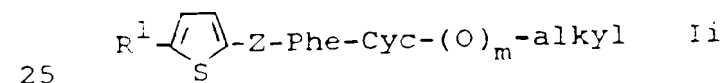
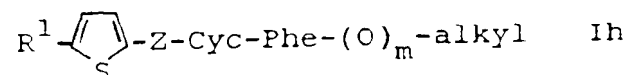
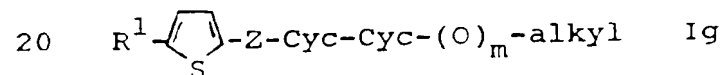
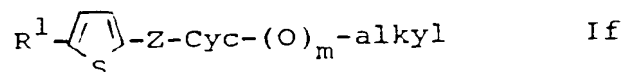
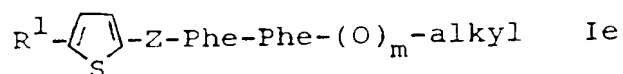
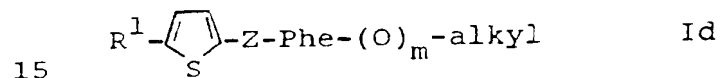
The compounds of the formula I have a wide range of  
20 application. Depending on the choice of the substituents, these compounds can be used as the base materials from which liquid crystalline mixtures are composed up to 50 % of the total constituents; however, it is also possible for compounds of the formula I to be added  
25 to liquid crystalline base materials of other classes of compounds, in order to influence the optical anisotropy of such a dielectric.

The invention thus relates to alkylthiophenes of formula I,  
5 in particular to

alkylthiophenes selected from the formulae Ia to Ic:



alkylthiophenes selected from the formulae Id to Ii:







Furthermore the invention relates to liquid crystalline media with at least two components characterized in that at least one component is a compound of the formula I. The invention relates furthermore to electro-optic display devices containing such media.

Above and below,  $R^1$ ,  $R^2$ ,  $R$ ,  $n$ ,  $m$ ,  $X$ ,  $A$ ,  $Z$ ,  $Cyc$  and  $Phe$   
10 have the meaning given, unless expressly indicated  
otherwise.

The compounds of the formula I accordingly include preferred compounds with two rings of the part formula II:






and compounds with three rings of part formulae 12



In the compounds above and below R<sup>1</sup> preferably denotes  
20 alkyl, R<sup>2</sup> preferably denotes F, CN or alkyl, or further-  
more alkoxy.

Z is preferably a -CO-O-, or -CH<sub>2</sub>CH<sub>2</sub>-group. Particularly preferred are compounds wherein Z denotes -CO-O-. In the compounds of the formula I wherein n is 2 the group

-  - may be equal or different. -  -  -, there-

fore denotes preferably Cyc-Cyc or Phe-Phe, furthermore preferred Phe-Cyc or Cyc-Phe.

If  $R^1$  and/or  $R^2$  are an alkyl residue and/or alkoxy radical, this radical can be straight-chain or branched. Preferably, it is straight-chain and has 2, 3, 4, 5, 6 or 7 C atoms and is accordingly preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy or heptyloxy, also methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tridecyloxy or tetradecyloxy.

Oxaalkyl is preferably straight-chain 2-oxapropyl (= methoxymethyl), 2-(= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6-, or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

If  $R^2$  is an alkenyl residue, it can be straight-chain or branched. Preferably, it is straight-chain and has 2 to 10 C atoms. It is accordingly, in particular, vinyl, prop-1- or prop-2-enyl, but-1-, -2- or -3-enyl, pent-1-, -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5- or -6-enyl, oct-1-, -2-, -3-, -4-, -5-, -6- or -7-enyl, non-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-enyl or dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8- or -9-enyl.

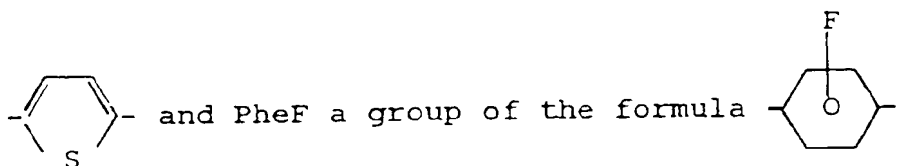
Compounds of the formula I with branched terminal groups  $R^2$  can occasionally be of importance because of an improved solubility in the customary liquid crystal base materials, but in particular as chiral doping substances if they are optically active.

Branched groups of this type as a rule contain not more than one chain branching. Preferred branched residues  $R^2$  are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy and 1-methylheptoxy.

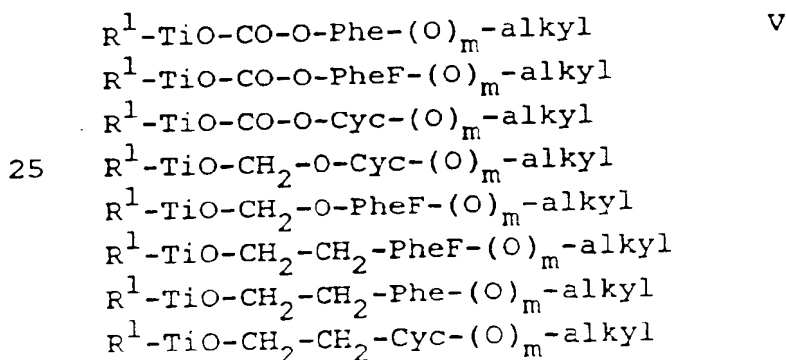
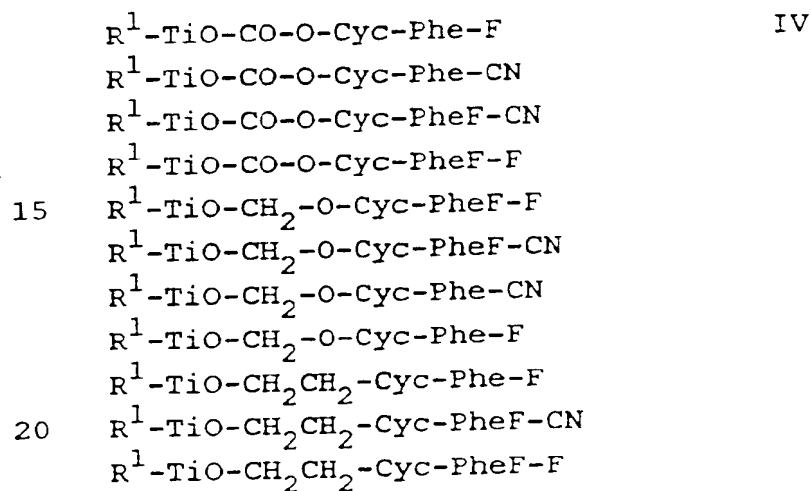
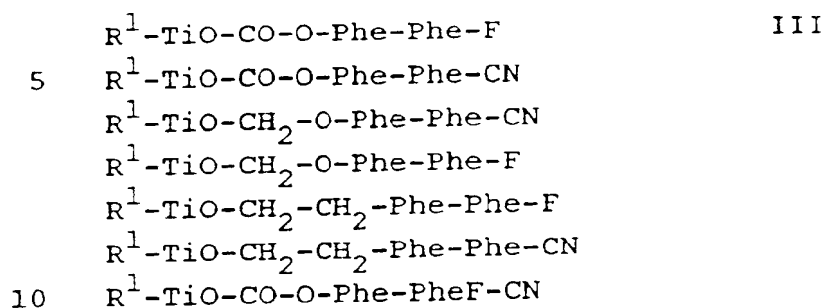
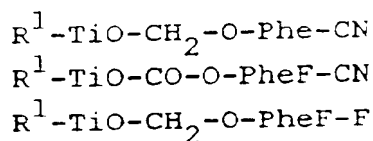
Formula I includes both the racemates of these compounds and the optical antipodes, as well as mixtures thereof.

Those of the compounds of the formulae I, Ia to II in which at least one of the radicals contained therein has one of the preferred meanings mentioned are preferred.

Particular preferred compounds of the formula I are those of the following groups II to IX in which TiO denotes a group of the formula



- 25  $R^1$ -TiO-CO-O-Phe-F  
 $R^1$ -TiO-CO-O-Phe-CN  
 $R^1$ -TiO-CH<sub>2</sub>-O-Phe-CN  
 $R^1$ -TiO-CO-O-PheF-F  
 $R^1$ -TiO-CH<sub>2</sub>-O-Phe-F
- II



- $R^1$ -TiO-CO-O-Phe-Phe-(O)<sub>m</sub>-alkyl VI  
 $R^1$ -TiO-CO-O-Phe-PheF-(O)<sub>m</sub>-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-O-Phe-PheF-(O)<sub>m</sub>-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-O-Phe-Phe-(O)<sub>m</sub>-alkyl  
 5  $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-Phe-Phe-(O)<sub>m</sub>-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-Phe-PheF-(O)<sub>m</sub>-alkyl  
  
 $R^1$ -TiO-CO-O-Cyc-Cyc-alkyl VII  
 $R^1$ -TiO-CH<sub>2</sub>-O-Cyc-Cyc-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-Cyc-Cyc-alkyl  
  
 10  $R^1$ -TiO-CO-O-Phe-Cyc-alkyl VIII  
 $R^1$ -TiO-CO-O-PheF-Cyc-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-O-PheF-Cyc-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-O-Phe-Cyc-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-Phe-Cyc-alkyl  
 15  $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-PheF-Cyc-alkyl  
  
 $R^1$ -TiO-CO-O-Cyc-Phe-(O)<sub>m</sub>-alkyl IX  
 $R^1$ -TiO-CO-O-Cyc-PheF-(O)<sub>m</sub>-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-O-Cyc-PheF-(O)<sub>m</sub>-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-O-Cyc-Phe-(O)<sub>m</sub>-alkyl  
 20  $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-Cyc-Phe-(O)<sub>m</sub>-alkyl  
 $R^1$ -TiO-CH<sub>2</sub>-CH<sub>2</sub>-Cyc-PheF-(O)<sub>m</sub>-alkyl

In the compounds of the formula I, those stereoisomers in which the rings Cyc are trans-1,4-disubstituted are preferred.

- 25 The compounds of the formula I are prepared by methods which are known per se, such as are described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der Organischen Chemie [Methods

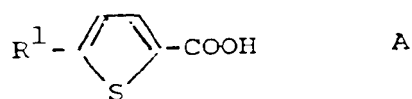
of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), and in particular under reaction conditions which are known and suitable for the reactions mentioned in more detail here can also be used in this connection.

- 5 If desired, the starting substances can also be formed in situ, such that they are not isolated from the reaction mixture but are immediately reacted further to give the compounds of the formula I.

- 10 Esters of the formula I can be obtained by esterification of corresponding carboxylic acids (or their reactive derivatives) with alcohols or phenols (or their reactive derivatives), preferably with dicyclohexylcarbodiimide as dehydrating agent.

- 15 The corresponding carboxylic acids and alcohols or phenols are known or can be prepared by processes analogous to known processes.

The thiophene-carboxylic acids of the formula A



- 20 can be prepared as described, for example, by J.M. Barker and P.R. Huddleston in Heterocyclic Chemistry "Thiophene and its Derivatives", Part III.

- 25 Particularly suitable reactive derivatives of the carboxylic acids mentioned are the acid halides, above all the chlorides and bromides, and furthermore the anhydrides, for example also mixed anhydrides, preferably those of the corresponding carboxylic acids and trifluoroacetic acid formed in situ by mixing these carboxylic acids with

trifluoroacetic anhydride, azides or esters, in particular alkyl esters with 1-4 C atoms in the alkyl group.

Possible reactive derivatives of the alcohols or phenols mentioned are, in particular, the corresponding metal  
5 alcoholates or phenolates, preferably of an alkali metal, such as sodium or potassium.

The esterification is advantageously carried out in the presence of an inert solvent. Particularly suitable  
10 solvents are ethers, such as diethyl ether, di-n-butyl ether, THF, dioxane or anisole, ketones, such as acetone, butanone or cyclohexanone, amides, such as dimethylformamide or phosphoric acid hexamethyltri-  
15 amide, hydrocarbons, such as benzene, toluene or xylene, halogenohydrocarbons, such as carbon tetrachloride or tetrachloroethylene, and sulfoxides, such as dimethylsulfoxide or sulfolane. Water-immiscible solvents can simultaneously be advantageously used for azeotropic distillation of the water formed during the esterification. An excess of an organic base, for example pyridine, quinoline or triethylamine, can  
20 occasionally also be used as the solvent for the esterification. The esterification can also be carried out in the absence of a solvent, for example by heating the components in the presence of sodium acetate. The reaction temperature is usually between  $-50^{\circ}$  and  $+250^{\circ}$ , preferably between  $-20^{\circ}$   
25 and  $+80^{\circ}$ . At these temperatures, the esterification reactions have as a rule ended after 15 minutes to 48 hours.

In detail, the reaction conditions for the esterification depend largely on the nature of the starting substances used. Thus, a free carboxylic acid is as a rule reacted  
30 with a free alcohol or phenol in the presence of a strong acid, for example a mineral acid, such as hydrochloric acid or sulfuric acid. A preferred reaction procedure is

20

30



sulfate, preferably in an inert solvent, such as acetone, 1,3-dimethoxyethane, DMF or dimethyl sulfoxide, or an excess of aqueous or aqueous-alcoholic NaOH or KOH, at temperatures between about 20 ° and 100 °C.

- 5 The ethane derivatives of the formula I ( $Z = \text{CH}_2\text{CH}_2$ ) can be prepared by reducing a compound which otherwise corresponds to the formula I but contains a  $-\text{CH}_2\text{CO}-$ ,  $-\text{CO}-\text{CH}_2-$  or  $-\text{CH}=\text{CH}-$ group instead of a  $-\text{CH}_2-\text{CH}_2-$ group.

These ketones can be reduced, for example, by the method of Clemmensen (with zinc, zinc analogam or tin and hydrochloric acid, advantageously in aqueous-alcoholic solution or in a heterogenous phase with water/toluene at temperatures between 80 and 120 °), Wolff-Kishner (with hydrazine, advantageously in the presence of alkali, such as KOH or NaOH, in a high boiling solvent at temperatures between 100 and 200 °) or Huang-Minlon modification (analogously Wolff-Kishner but in refluxing diethylene glycol).

20 The intermediates wherein Z denotes  $-\text{CO}-\text{CH}_2-$  can be obtained by Friedel-Crafts acylation of 2-alkylthiophene with compounds of the formula



halogen, preferably chlorine, as described analogously,  
25 for example, by J.R. Johnson, C.E. May in Organic  
Synthesis Coll. Voll. III, p. 8 to 9).

As well as one or more compounds according to the invention, the nematic liquid-crystal media according to the invention preferably contain, as further constituents, 2 to 40, in particular 4 to 30, components. Very particularly preferably these media contain 7 to 25 components as well as one or more compounds according to the invention. These further constituents are preferably selected from nematic or nematogenic (monotropic or isotropic) substances, in particular substances belonging to the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenyl or cyclohexyl cyclohexylbenzoates, phenyl or cyclohexyl cyclohexylcyclohexanecarboxylates, cyclohexylphenyl benzoates, cyclohexanecarboxylic acid or cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenylpyrimidines, cyclohexylpyrimidines, phenylpyridines, cyclohexylpyridines, phenyldioxanes, cyclohexyldioxanes, phenyl-1,3-dithianes, cyclohexyl-1,4-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)-ethanes, 1-cyclohexyl-2-biphenylylethanes, 1-phenyl-2-cyclohexylphenylethanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The 1,4-phenylene groups in these compounds can also be fluorinated.

The most important compounds which are suitable for use are further constituents of nematic media according to the invention can be characterized by means of the formulae 1, 2, 3, 4 and 5:

5	$R'-L-E-R''$	1
	$R'-L-COO-E-R''$	2
	$R'-L-OOC-E-R''$	3
	$R'-L-CH_2CH_2-E-R''$	4
	$R'-L-C\equiv C-E-R''$	5

10 In the formulae 1, 2, 3, 4 and 5 L and E, which can be identical or different, independently of one another are each a divalent radical belonging to the group composed of -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-,  
15 -Dio-, -G-Phe- and -G-Cyc- and mirror images thereof, Phe being 1,4-phenylene which is unsubstituted or substituted by fluorine, Cyc being trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr being pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio being 1,3-dioxane-2,5-diyl and G being 2-(trans-1,4-cyclohexy)-ethyl, pyrimidine-  
20 2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

Preferably, one of the radicals L and E is Cyc, Phe or Pyr. E is preferably Cyc, Phe or Phe-Cyc. The media according to the invention preferably contain one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which L and E are selected from the group comprising Cyc, Phe and Pyr, and, at the same time, one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which one of the radicals L and E is selected from the group comprising Cyc, Phe or Pyr and the other radical is selected from the group comprising -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G-Phe and -G-Cyc-, and, if appropriate,

one ore more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which the radicals L and E are selected from the group comprising -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-.

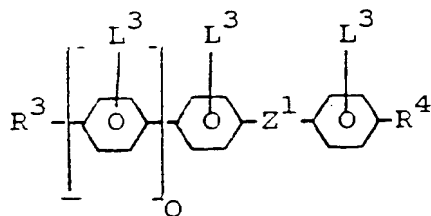
- 5 In the compounds of the partial formulae 1a, 2a, 3a, 4a and 5a R' and R" independently of one another are each alkyl, alkenyl, alkoxy, alkenyloxy or alkanoyloxy having up to 8 carbon atoms. In most of these compounds R' and R" are different from one another, one of these radicals  
10 being alkyl or alkenyl in most cases. In the compounds of the partial formulae 1b, 2b, 3b, 4b and 5b R" is -CN, -CF<sub>3</sub>, F, Cl or -NCS; R in this case has the meaning indicated for the compounds of the partial formulae 1a to 5a and is prefereably alkyl or alkenyl. Other variants of the  
15 substituents envisaged are also customary, however, in the compounds of the formulae 1, 2, 3, 4 and 5. Many substances of this type or mixtures thereof are commercially available. All these substances can be obtained by methods known from the literature or analogously thereto.
- 20 As well as components belonging to the group of the compounds 1a, 2a, 3a, 4a and 5a (Group 1), the media according to the invention also preferably contain components belonging to the group of the compounds 1b, 2b, 3b, 4b and 5b (Group 2), and the proportions thereof  
25 are preferably as follows:

Group 1: 20 to 90 %, especially 30 to 90 %,  
Group 2: 10 to 80 %, especially 10 to 50 %,

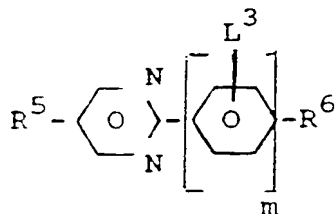
- the sum of the proportions of the compounds according to the invention and of the compounds belonging to  
30 Groups 1 and 2 adding up to 100 %.

The nematic media according to the invention preferably contain 1 to 40 %, particularly preferably 5 to 30 %, of compounds according to the invention. Media containing more than 40 %, in particular 45 to 90 %, of compounds according to the invention are also preferred. the media preferably contain three, four or five compounds according to the invention.

Particularly preferred chiral tilted smectic liquid crystal media according to the invention are those in which the achiral base mixture contains, in addition to compounds of the formula I, preferably of the formulae Id to Ii, at least one other component with a negative or comparatively low positive dielectric anisotropy. This/these other component(s) of the achiral base mixture can make up 10 to 99 %, preferably 50 to 95 %, of the base mixture. Suitable further components with a comparatively low positive or negative dielectric anisotropy are compounds of the formulae 6 to 10.



6



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with in each case 5 to 10 C atoms.

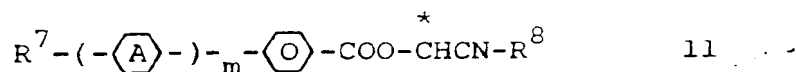
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Preferred chiral dopants are those of formula 11



wherein  $R^7$  is alkyl or alkoxy with 5 to 15 C atoms.  $R^8$  is alkyl with 1 to 8 C atoms, m is 1 or 2, and - A - is 1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl or trans-1,4-cyclohexylene.

The preparation of the media according to the invention is effected in a manner customary per se. As a rule, the components are dissolved in one another, preferably at an elevated temperature. The liquid-crystal phases according to the invention can be modified by means of suitable additives so that they can be used in any type of liquid-crystal display elements hitherto disclosed. Additives of this type are known to those skilled in the art and are described in detail in the literature (H. Kelker/R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980). For example, pleochroic dyes can be added in order to prepare coloured guest-host systems, or substances can be added to alter the dielectric anisotropy, the viscosity and/or the orientation of the nematic phases.

The following examples are intended to illustrate the invention without limiting it. M.P. = melting point and c.p. = clear point. In the preceding and following text percentages are per cent by weight; all temperatures are quoted in degrees centigrade. "Customary working up" means as follows: water is added, the mixture is extracted with methylene chloride, the phases are separated, the organic phase is dried and evaporated and the product is purified by crystallization and/or chromatography.



5

### Example 1

Preparation of 4-Cyanophenyl 5-n-propylthiophene-2-carboxylate

10

20

- 25

4-n-Butyloxyphenyl 5-n-pentylthiophene-2-carboxylate  
4-n-Butyloxyphenyl 5-n-hexylthiophene-2-carboxylate  
4-n-Butyloxyphenyl 5-n-heptylthiophene-2-carboxylate  
4-n-Butyloxyphenyl 5-n-octylthiophene-2-carboxylate

4-n-Pentylphenyl 5-ethylthiophene-2-carboxylate  
4-n-Pentylphenyl 5-n-propylthiophene-2-carboxylate  
4-n-Pentylphenyl 5-n-butylthiophene-2-carboxylate  
4-n-Pentylphenyl 5-n-pentylthiophene-2-carboxylate  
4-n-Pentylphenyl 5-n-hexylthiophene-2-carboxylate  
4-n-Pentylphenyl 5-n-heptylthiophene-2-carboxylate

4-n-Octyloxyphenyl	5-ethylthiophene-2-carboxylate
4-n-Octyloxyphenyl	5-n-propylthiophene-2-carboxylate
4-n-Octyloxyphenyl	5-n-butylthiophene-2-carboxylate
4-n-Octyloxyphenyl	5-n-pentylthiophene-2-carboxylate
4-n-Octyloxyphenyl	5-n-hexylthiophene-2-carboxylate
4-n-Octyloxyphenyl	5-n-heptylthiophene-2-carboxylate
4-n-Octyloxyphenyl	5-n-octylthiophene-2-carboxylate

The following compound are obtained analogously using 4'-substituted biphenyl-4-ols as starting material:

4'-Cyanobiphenyl-4-yl 5-ethylthiophene-2-carboxylate  
4'-Cyanobiphenyl-4-yl 5-n-propylthiophene-2-carboxylate,  
C 133.1 N 290.1 I  
4'-Cyanobiphenyl-4-yl 5-n-butylthiophene-2-carboxylate  
4'-Cyanobiphenyl-4-yl 5-n-pentylthiophene-2-carboxylate

4'-Cyanobiphenyl-4-yl 5-n-hexylthiophene-2-carboxylate  
4'-Cyanobiphenyl-4-yl 5-n-heptylthiophene-2-carboxylate  
4'-Cyanobiphenyl-4-yl 5-n-octylthiophene-2-carboxylate

4'-n-Pentylbiphenyl-4-yl 5-ethylthiophene-2-carboxylate

5 4'-n-Pentybiphenyl-4-yl 5-n-propylthiophene-2-carboxylate,  
C 95.9 N 125.9 I

4'-n-Phenylbiphenyl-4-yl 5-n-butylthiophene-2-carboxylate

4'-n-Phenylbiphenyl-4-yl 5-n-pentylthiophene-2-carboxylate

4'-n-Phenylbiphenyl-4-yl 5-n-hexylthiophene-2-carboxylate

10 4'-n-Phenylbiphenyl-4-yl 5-n-heptylthiophene-2-carboxylate

4'-n-Phenylbiphenyl-4-yl 5-n-octylthiophene-2-carboxylate

4'-n-Phenylbiphenyl-4-yl 5-n-nonylthiophene-2-carboxylate

4'-n-Phenylbiphenyl-4-yl 5-n-dodecylthiophene-2-carboxylate

4'-n-Octyloxybiphenyl-4-yl 5-ethylthiophene-2-carboxylate

15 4'-n-Octyloxybiphenyl-4-yl 5-n-pentylthiophene-2-carboxylate

4'-n-Octyloxybiphenyl-4-yl 5-n-octylthiophene-2-carboxylate

4'-n-Octyloxybiphenyl-4-yl 5-n-nonylthiophene-2-carboxylate

4'-n-Octyloxybiphenyl-4-yl 5-n-dodecylthiophene-2-carboxylate

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-ethylthiophene-2-  
20 carboxylate

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-propylthiophene-2-carboxylate, C 73.2 N, 118.3 I

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-butylthiophene-2-carboxylate

25 4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-pentylthiophene-2-  
carboxylate

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-hexylthiophene-2-carboxylate

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-heptylthiophene-2-  
30 carboxylate

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-octylthiophene-2-carboxylate

4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-nonylthiophene-2-carboxylate

5 4'-n-Octyloxy-3'-fluorobiphenyl-4-yl 5-n-dodecylthiophene-2-carboxylate

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-ethylthiophene-2-carboxylate

10 4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-propylthiophene-2-carboxylate

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-butylthiophene-2-carboxylate

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-pentylthiophene-2-carboxylate

15 4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-hexylthiophene-2-carboxylate

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-heptylthiophene-2-carboxylate

20 4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-octylthiophene-2-carboxylate

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-nonylthiophene-2-carboxylate, C 37.8, S<sub>C</sub> 50.6, N 77.9 I

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-decylthiophene-2-carboxylate

25 4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-undecylthiophene-2-carboxylate

4'-n-Nonyl-2-fluorobiphenyl-4-yl 5-n-dodecylthiophene-2-carboxylate, C 48.7, S<sub>C</sub> 75.7, S<sub>A</sub> 76.3, N 78.3 I

The following compounds are obtained analogously using 4'-substituted bicyclohexan-4-ols as starting material:

- trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-ethylthiophene-2-carboxylate
- 5 trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-propylthiophene-2-carboxylate, C 59.4 S 98.2 N 147.1 I
- trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-butylthiophene-2-carboxylate
- trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-pentylthiophene-2-carboxylate
- 10 trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-hexylthiophene-2-carboxylate
- trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-heptylthiophene-2-carboxylate
- 15 trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-octylthiophene-2-carboxylate
- trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-nonylthiophene-2-carboxylate
- trans,trans-4'-n-Pentylbicyclohexyl-4-yl 5-n-dodecylthiophene-2-carboxylate
- 20

#### Example 2

Preparation of 1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-pentylbicyclohexyl-4-yl)ethane

- A. 1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-pentyl-bicyclohexyl-4-yl)ethan-1-one:
- 25

Freshly distilled stannic chloride (0.2 mol) is added dropwise at 0 °C to a mixture of 2-n-propylthiophene (0.2 mol), 2-(trans,trans-4'-n-pentylbicyclohexyl-4-yl)acetyl chloride (0.2 mol) and dry 1,2-dichloroethane (200 ml). After all the

30

5 stannic chloride has been added the mixture is stirred at room temperature for two hours. The addition product is hydrolyzed by the slow addition of a mixture of water and concentrated hydrochloric acid (9:1). The organic layer is separated, washed with water and dried over anhydrous calcium chloride. After all the organic solvent has been evaporated the crude product is reacted without further purification.

10 B. Huang Minlon reduction

15 A mixture of crude product A (0.1 mol) and hydrazine hydrate (0.5 mol) in diethylene glycol (200 ml) is heated for a period of 2.5 hrs during which the temperature is slowly raised to 210 °C. After cooling potassium hydroxide (0.5 mol) is added and the reaction mixture is refluxed at 145 °C for 1 hour.

20 After cooling to room temperature water (250 ml) is added and the reaction mixture is extracted with chloroform (3 x 100 ml) and washed with aqueous hydrochloric acid (2 M, 100 ml), saturated sodium bicarbonate (100 ml), water 100 ml and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After purifying by chromatography and crystallization 1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-pentylbicyclohexyl-4-yl)ethane is obtained exhibiting a viscosity of 22.6 cst (20 °C)

25

Analogously are obtained:

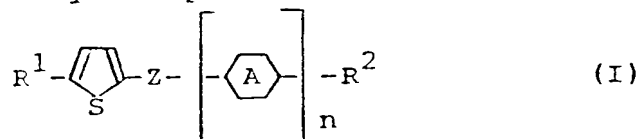
- 1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-ethyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-propyl-  
5 bicyclohexyl-4-yl)ethane  
1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-butyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-hexyl-  
bicyclohexyl-4-yl)ethane  
10 1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-heptyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-octyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-nonyl-  
15 bicyclohexyl-4-yl)ethane  
1-(5-n-Propylthiophen-2-yl)-2-(trans,trans-4'-n-dodecyl-  
bicyclohexyl-4-yl)ethane
- 1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-ethyl-  
bicyclohexyl-4-yl)ethane  
20 1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-propyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-butyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-hexyl-  
25 bicyclohexyl-4-yl)ethane  
1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-heptyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-octyl-  
bicyclohexyl-4-yl)ethane  
30 1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-nonyl-  
bicyclohexyl-4-yl)ethane  
1-(5-n-Nonylthiophen-2-yl)-2-(trans,trans-4'-n-dodecyl-  
bicyclohexyl-4-yl)ethane





## Claims

1. Alkylthiophenes of the formula I



5 wherein

$R^1$  is alkyl with up to 16 C atoms wherein one  $\text{CH}_2$  group may be replaced by  $-\text{O}-$ ,

10  $R^2$  is X or an alkyl or alkenyl residue each with up to 16 C atoms wherein one or two non-adjacent  $\text{CH}_2$  groups of these residues may be replaced by  $-\text{O}-$ ,  $-\text{CO}-\text{O}-$  or  $-\text{O}-\text{CO}-$ ,

Z is  $-\text{CO}-\text{O}-$ ,  $-\text{O}-\text{CO}-$ ,  $-\text{CH}_2-\text{O}-$  or  $-\text{CH}_2\text{CH}_2-$ ,

$-\text{C}_6\text{H}_4\text{A}-$  is Cyc or Phe,

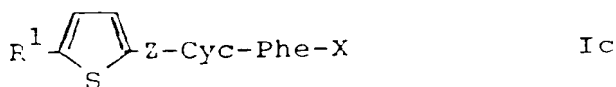
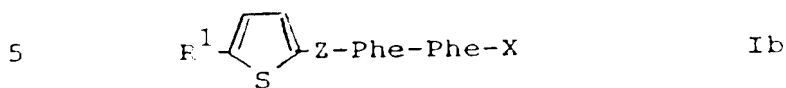
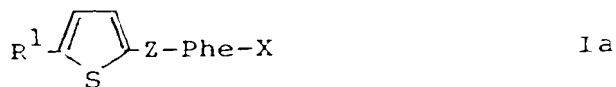
Cyc is trans-1,4-cyclohexylene,

15 Phe is 1,4-phenylene optionally substituted by fluorine or methyl groups,

X is F or CN, and

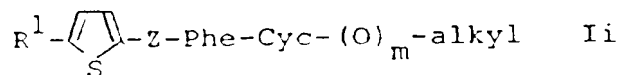
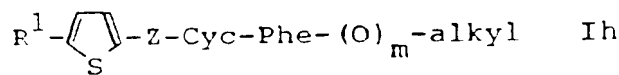
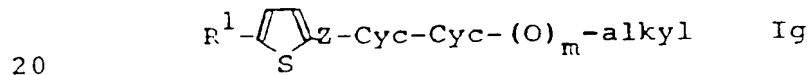
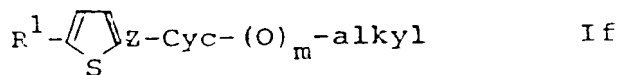
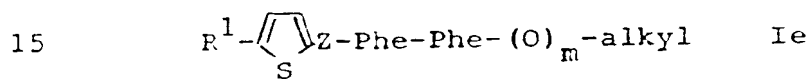
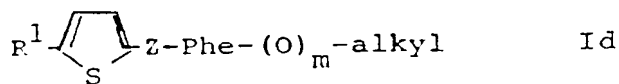
n is 1 or 2.

2. Alkylthiophenes according to claim 1 selected from the formulae Ia to Ic:



10 wherein  $\text{R}^1$ , Z, Cyc, Phe and X have the meaning given in claim 1.

3. Alkylthiophenes according to claim 1 selected from the formulae Id to Ii:



wherein  $R^1$ , Z, Phe and Cyc have the meaning given in claim 1, and alkyl denotes an alkyl residue with up to 16 C atoms and

m is 0 or 1.

- 5 4. Liquid crystalline medium having at least two liquid crystalline components, characterized in that at least one component is an alkylthiophene according to claim 1.
- 10 5. Nematic liquid crystalline medium according to claim 4, characterized in that at least one component is an alkylthiophene according to claim 2.
6. Smectic liquid crystalline medium according to claim 4, characterized in that at least one component is an alkylthiophene according to claim 3.
- 15 7. Electrooptical display device, characterized in that it contains a medium according to claim 4.
8. Twisted nematic cell, characterized in that it contains a medium according to claim 5.
- 20 9. Electrooptical display device based on the principle of SSFLC technology, characterized in that it contains a medium according to claim 6.

